

REMARKS

Claims 20 and 24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Fusegawa et al. (US 2003/0106484) (hereinafter: "Fusegawa") in view of JP 2003-297840 (hereinafter "JP '840"). Claims 21, 22, 25, 26, 28-30, 32-34, 36-38 and 40-45 are rejected under 35 U.S.C. 103(a) as being unpatentable over Fusegawa and JP '840 and further in view of various combinations of Haas et al. (US 4,119,441) (hereinafter: "Haas"), Asayama et al. (U.S. Patent No. 6,641,888) (hereinafter: "Asayama") and Momoi et al. (U.S. Patent No. 2002/0024152) (hereinafter: "Momoi").

The Office identifies Fusegawa as disclosing a silicon wafer manufactured from a silicon single crystal having high interstitial oxygen concentration as recited in claims 20 and 24. JP '840 is cited as disclosing a relational expression between an interstitial oxygen concentration and heat treatment temperature as recited in claims 20 and 24. The remaining references are cited as disclosing various of the limitations of the remaining claims.

Applicants respectfully submit that the proposed combination of Fusegawa with JP '840 and the combination of Fusegawa with JP '840 and other prior art including the references cited in the Action will not result in the method of the present invention as recited in the rejected claims.

The present invention relates to an interstitial oxygen concentration and heat treatment temperature meeting the conditions of the following expression:

$$[O_i] \leq 2.123 \times 10^{21} \exp (-1.035/k(T+273))$$

The expression is different and not obvious from the expression disclosed in JP 2003-297840.

Fusegawa shows the Czochralski (crystal pulling) method and discloses a method for making the interstitial oxygen concentration in the single silicon crystal low by controlling the pulling conditions (pulling speed, strength of magnetic field, for single crystal silicon, rotary speed of crucible, etc.) and manufacturing high quality wafers. Furthermore, Fusegawa discloses heat treatment of this wafer for 100 minutes at 1150°C in a wet oxidizing atmosphere to examine the distribution of OSF occurrence in a wafer grown and manufactured under the conditions prescribed above. In addition, it is disclosed that from the standpoint of warp and slippage, the preferable oxygen concentration for the wafer described above is $6 - 10 \times 10^{17}$ atom/cm³.

As noted by the Office, Fusegawa does not disclose a relationship between the interstitial oxygen concentration of the

wafer and the heat treatment temperature for the wafer. In addition, no SOI wafer manufacturing method is disclosed.

Fusegawa describes a method for pulling a crystal without including COPs, keeping the oxygen concentration low and making the BMDs in the wafer surface uniform. The invention of the present application is a method that pulls a crystal that includes COPs, cuts out the wafer, and eliminates the COPs by heat treatment in an oxidizing atmosphere at a temperature relating to the wafer oxygen concentration. Therefore, the present application and Fusegawa are completely different inventions.

In JP '840, heat treating a silicon wafer at a temperature that satisfies the following expression is disclosed. This expression shows the relationship between oxygen concentration and temperature.

$$[O_i] < 10 \cdot F(T) \exp\left(-\frac{2\sigma_{SiO_2}}{RT}\right)$$

(wherein σ_{SiO_2} is the surface energy of silicon oxide).

In other words, the expression disclosed in JP '840 includes the thermal equilibrium concentration (solid solubility) $[O_i]^{eq}$ of the interstitial oxygen. According to paragraph [0022] of the reference:

"[O_i]^{eq}(T) is the edge solubility (Randloeslichkeit) of the oxygen in the silicon at a given temperature T. Functions of this sort are discussed in Hull, R. (Ed.), "Properties of Crystalline Silicon," The Institution of Electrical Engineers, London, 1999, p. 489 ff."

Attached hereto is a copy of "Properties of Crystalline Silicon" referred to in JP '840. On p. 489, it is written that:

$$[O_{i,eq}]_{sol} = C_{so} \exp(-E_s(K)/T) \text{ cm}^{-3}.$$

The values of C_{so} and E_s are in TABLE 1 on p. 490. C_{so} and E_s differ according to the reporter, and 11 combinations are given in TABLE 1 on p. 490. In other words, in JP '840, the range of [O_i] is uncertain.

Thus, JP '840 fails to disclose or suggest the expression relating interstitial oxygen concentration and temperature recited in the present application, i.e.:

$$[O_i] < 2.123 \times 10^{21} \exp(-1.035/k(T + 273))$$

Therefore, the combination of Fusegawa and JP '840 will not result in the method recited in the present application.

Regarding other references cited by the Office, in Haas, a technique for P doping using neutron irradiation in a manufacturing method for single crystals of silicon is disclosed. There is no

disclosure concerning wafer oxygen concentration and heat treatment temperatures for wafers.

Asayama discloses the doping of a prescribed concentration of nitrogen and a prescribed concentration of carbon in single crystal silicon for silicon wafers and epitaxial wafers. The relationship between the oxygen concentration of those silicon wafers and heat treatment temperatures is not disclosed.

In Momoi, a SOI manufacturing method is disclosed. Nothing is described concerning the relationship between heat treatment temperatures and oxygen concentration.

Conversely, the invention of the present application has been established based on the expression described above regarding the relationship between the oxygen concentration of the silicon wafer and the heat treatment temperature in the manufacturing of a silicon wafer. This relationship is not disclosed or suggested in any of Fusegawa, JP '840, Haas, Asayama and Momoi, taken alone or in any combination.

It is noted that in Fusegawa, in particular, the reason for setting a prescribed value for the interstitial oxygen concentration in single crystal silicon is to prevent the occurrence of warpage when heat treatment is later carried out on the wafer. In addition, the heat treatment is also to prevent the

occurrence of slip dislocation because of thermal strain. In other words, no relationship between the heat treatment temperature in heat treatment and the oxygen concentration in the wafer in the manufacturing of silicon wafers is disclosed, explicitly or inherently, or suggested in Fusegawa.

As noted above, JP '840 fails to disclose or suggest the mathematical relationship recited in the claims of the present application.

Therefore, even if a person of ordinary skill in the art would have been motivated to combine of the invention of Fusegawa with the teachings of JP '840, and even if a further combination of the teachings of Haas, and/or the teachings of Asayama, and/or the teachings of Momoi is made, the combination(s) will not result in the method recited in the claims of the present application.

For the above reasons, removal of the 35 U.S.C. 103(a) rejections of the claims is believed to be in order and is respectfully requested.

The foregoing is believed to be a complete and proper response to the Office Action dated July 26, 2007, and is believed to place this application in condition for allowance. If, however, issues remain that can be resolved by means of a telephone interview, the

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RESPONSE UNDER 37 C.F.R. §1.111

**PATENT
NON-FINAL**

Examiner is respectfully requested to contact the undersigned attorney at the telephone number indicated below.

In the event that this paper is not considered to be timely filed, applicants hereby petition for an appropriate extension of time. The fee for any such extension may be charged to our Deposit Account No. 111833.

In the event any additional fees are required, please also charge our Deposit Account No. 111833.

Respectfully submitted,

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Attachments: "Properties of Crystalline Silicon"

9.3 Solubility of O in c-Si

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A INTRODUCTION

In the Czochralski (CZ) growth, O is introduced in molten silicon from the dissociation of silica from the crucible. It can also be introduced during float-zone (FZ) growth when O-bearing gases are used, or by solid state diffusion.

The measurement of a solubility is that of a maximum concentration of isolated O in liquid or solid silicon under equilibrium with silicon oxides at a given temperature. Direct measurements of the O concentration in molten silicon contained in a silica crucible have recently been made using an electrochemical O sensor [1,2]. Common methods used to derive an O concentration are applicable only for the solid state. They are:

- Charged particle activation analysis (CPAA)
- Secondary ion mass spectroscopy (SIMS)
- Gas fusion analysis (GFA)
- Infrared (IR) absorption

CPAA, SIMS and GFA allow the determination of the overall O concentration. IR absorption is used to measure the concentration of interstitial oxygen atoms bonded to two nearest neighbour Si atoms (O₂). The IR method is based on the fact that the normal cooling rate of CZ silicon is too fast for noticeable precipitation of silicon oxides to occur so that metastable O₂ concentrations comparable to the ones near the melting point (1413°C) are measured. The O₂ concentration is determined from the room temperature absorption coefficient of an O₂ vibration-rotation band at 9.04 μm using a suitable calibration factor. Within ±3%, there is now a world-wide agreement on a value of $3.1 \times 10^{17} \text{ cm}^{-3}$ for this factor [3]. Silica precipitates may be present in the crystal for very high oxygen concentrations or after some annealing treatments. They can alter the measurement as they show absorption in the same spectral region as the O₂ band. An alternative in that case is to measure the absorption near liquid helium temperature (LHeT) [4]. Another one is to measure at room temperature a weak absorption band of O₂ at 5.81 μm or 1720 cm⁻¹ in wavenumber, which is free of interference with the absorption of the precipitates [5]. Another method for O₂ determination is to measure, by an X-ray technique, the average lattice expansion due to the presence of O₂ in the crystal [6]. The lattice expansion coefficient β can be expressed in terms of the increase Δa₀ of the lattice constant due to an increase ΔN of the concentration of a foreign atom as Δa₀/(a₀ΔN). For O₂, a reliable value of β is $(4.4 \pm 0.2) \times 10^{-4} \text{ cm}^3$ [7].

B LIQUID SOLUBILITY

A determination of the liquid solubility from thermodynamic calculations has been made by Carlberg [9]. It is based on an experimental value of the standard free-energy of solution of oxygen in liquid silicon in equilibrium with SiO₂. The solubility is thermally activated and can be expressed as $[O]_{\text{eq}} = 1.3 \times 10^{18} \exp(-22370/(K)) \text{ cm}^{-3}$. The value at the melting point is found to be $2.1 \times 10^{14} \text{ cm}^{-3}$ and the activation energy 2.0 eV. Ekblut and Carlberg [9] have also shown the importance of the Si/SiO equilibrium in melts with a lower O content. Comparable results have been obtained experimentally by GFA of quenched melts contained in a silica tube by Hirata and

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Eschikawa [10] who derived $[O]_{\text{eq}} = 4.0 \times 10^{22} \exp(-2.0 \times 10^4/(K)) \text{ cm}^{-3}$. Huang et al [11] used GFA and SDAS to evaluate the O concentration in samples very similar to those of [8]. The main difference in their results is a much weaker temperature dependence of the solubility (if any). A value of the solubility in the melt near the melting point between $2 \text{ and } 3 \times 10^{18} \text{ cm}^{-3}$ seems a reasonable estimation.

The absolute values of the O concentrations obtained by direct measurements in a melt contained in a regular CZ crucible with an electrochemical O sensor [1] are larger than expected by about a factor of three. These values are very probably related to the method used, but the method gives significant evidence of an O concentration gradient related to the rotation of the crucible and to the O source (the concentration is larger near to the walls of the crucible than near to the centre). The existence of an O concentration gradient due to the rotation of the crucible is confirmed by IR determination of the radial distribution of O in different frozen melts by Togawa et al [12].

C SOLID SOLUBILITY

As-grown or as-quenched CZ silicon is oversaturated with O₂ at room temperature and the concentration measured is a good evaluation of the concentration near to the melting point. A reasonable order of magnitude of the solid solubility at the melting point can already be derived from the results of the quenched melt experiments in sealed quartz tubes indicating O₂ concentrations in the vicinity of $2 \times 10^{14} \text{ cm}^{-3}$. This figure has also been obtained from the construction of the Si-O phase diagram in the Si-rich region by Carlberg [8]. The O₂ concentration in CZ materials depends strongly on the growth parameters and it is generally less than the equilibrium solubility at the melting point. Precise adjustment of the growth parameters allows production of CZ silicon crystals with fairly uniform and controlled O concentrations. A review by Lin [13] on the incorporation of O shows that if usual growth parameters allow production of O₂ concentrations between about $5 \text{ and } 12 \times 10^{17} \text{ cm}^{-3}$, O₂ concentrations near to the solubility limit have been found in crystals grown with large crucible rotation rates (~30 rpm) or by applying a vertical magnetic field to the melt. The solubility is expected to decrease with temperature. Its measurement requires a physical situation where thermal equilibrium is reached at a given temperature. This has been typically done by annealing a CZ material at a given temperature to produce internal precipitation of silicon oxides or by making O diffuse at a given temperature in silicon with an initial low O₂ content, e.g. FZ silicon. The thermally activated solubility is expressed as:

$$[O]_{\text{eq}} = C_{\infty} \exp(-E_s/(K)) \text{ cm}^{-3} \quad (1)$$

where C_{∞} is a constant related to the entropy of solution and E_s the heat of solid solution in Kelvin ($E_s(\text{eV}) = 8.617 \times 10^{-5} E_s(\text{K})$). A summary of the results is presented in TABLE 1.

Part of the spreading of the experimental results has been analysed by Wilkes [22] as due to a combination of different factors including:

1. The difficulty in discriminating between the IR signatures of O₂ and of the precipitates.
2. Contamination of the samples.
3. Measurements performed while equilibrium was not reached.
4. Different IR calibration factors.

In 1986, Mäkelä [23] proposed a composite solubility curve yielding a heat of solution of 1.52 eV by bringing together experimental data from different origins. It corresponds to:

$$[O]_{\text{eq}} = 9.0 \times 10^{18} \exp(-1.76 \times 10^4/(K)) \text{ cm}^{-3} \quad (2)$$

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To obtain this expression, the data using IR measurements were regressed using a common IR calibration factor ($3.03 \times 10^{19} \text{ cm}^{-2} \text{ cm}^{-1}$) very close to the one recommended above. Thus, EQN (2) is recommended for the solubility of O in silicon, with a domain of validity between the silicon melting point and about 850°C. For these limits, the solubilities derived from EQN (2) are 2.58×10^{16} and $1.36 \times 10^{18} \text{ cm}^{-3}$, respectively. Between 850 and 700°C, the apparent solubility versus T^{-1} shows a flattening and Newman [24] even reports an increase of the solubility below 700°C to about 10^{17} cm^{-3} near 500°C. This is due to the combined increase of the concentration of oxide precipitates and to a decrease of their sizes and this must be considered as a pseudo-equilibrium situation.

TABLE 1 Summary of data relating to O solid solubility. E_g should be multiplied by 8.517×10^{-4} to read in eV.

E_g (eV)	C_s (10^{17} cm^{-3})	Temp. range (°C)	Method	Detection	Ref.
1.09	0.12	1000-1250	O precipitation	IR (LHeT)	[14]
2.67	18	1230-1400	Thermal desorption	Spreading resistance	[15]
1.82	12	1100-1200	O precipitation	IR (77 K)	[16]
1.39	0.82	"	O diffusion	X-rays	[6]
1.15	0.19	780-1100	O precipitation	IR (77 and 300 K)	[17]
1.24	0.28	1000-1230	O diffusion	CPAA	[18]
1.20	0.2	"	O precipitation in neutron-irradiated silicon	IR (300 K)	[19]
1.18	0.064	600-1240	O diffusion	SDAS and IR (300 K)	[20]
1.30	0.71	650-1050	O precipitation	IR (LHeT and 300 K)	[4]
1.49	0.95	1000-1375	O diffusion	CPAA	[21]
2.54	740	near 1413	O-Si phase diagram	"	[8]
1.62	2.6	850-1200	Compositional from [4], [16] and [20]	"	[4]

A decrease of the O solubility in n^+ Si-doped CZ silicon has been reported [25]. Possible reasons are: 1) a reduction of the O solubility in the melt due to antimony, 2) an increase of the O evaporation through Sb-containing oxides and 3) a decrease of the segregation of O. The measurements by Huang et al [11] of the O concentration in frozen melts containing increasing Sb concentrations show that for [Sb] < 1% at the O solubility is unchanged, but when [Sb] increases, the O solubility increases to reach about 10^{18} cm^{-3} for [Sb] near 2% at. These results seem to rule out the first assumption.

D CONCLUSION

A composite value of the O solubility in solid silicon $[O_s]_0$ at the melting point is $2.6 \times 10^{18} \text{ cm}^{-3}$, but in most CZ crystals, the maximum [O] measured in as-grown CZ silicon is $1.2-1.4 \times 10^{18} \text{ cm}^{-3}$ with a small concentration of precipitated [O] and TDs. Values near or slightly above the solubility limit have been found only in some 'magnetic' crystals [1], and this means that for most other CZ materials, the solubility limit is not reached. The above value of $[O_s]_0$ agrees acceptably with the value of $2.0 \times 10^{18} \text{ cm}^{-3}$ obtained from a determination of the Si/SiO₂ phase diagram.

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